



**ARIZONA DEPARTMENT OF TRANSPORTATION**  
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# **REACTIVE SILANE-COUPLED ASPHALT/MINERAL COMPOSITES AS BINDERS IN PAVING CONSTRUCTION**

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**December, 1983**

**Prepared for:**

Arizona department of Transportation  
206 South 17th Avenue  
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in cooperation with  
The U.S. Department of Transportation  
Federal Highway Administration

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16. Abstract  Composite materials using asphalts, mineral dusts, and a class of chemical coupling agents known as reactive silanes are prepared for use as binders in paving construction where asphalt alone is in general use at the present. The report describes how these coupling agents may, in very low concentrations, react with both asphalts and mineral dust fillers at the interfaces of their mixtures to integrate them into new materials which may appropriately be termed composite materials. Differing asphalts, mineral fillers, and silanes are considered. Also, wide ranges in composition and differing manufacturing methods are described. The report leads through a series of phases in development and characterization of composite products and in the evolution of the concepts and criteria felt by the author to be required for manufacture and control of superior composite binders.					
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## INTRODUCTION

### Background

Fillers are widely used in the plastics industry to reduce costs and to modify physical properties of products. In the case of thermoplastics, it is known that siliceous mineral fillers can have the effect of lowering strengths and other desirable physical properties in plastic/filler composites. This class of composites also have been known to be highly susceptible to loss of strength upon exposure to water. The unfavorable properties of siliceous fillers manifest themselves in spite of the great strengths, superior geometric features, and particle size options available in these fillers. This is attributed to the surface character of siliceous minerals, i.e., to an inherent incompatibility between the mineral surface and the organic polymer plastic and to the affinity of the mineral surface for water, known as hydrophilicity.

In thermoplastics, the disadvantages of siliceous mineral fillers can be overcome through the use of silane coupling agents. Silane coupling agents, or couplers, are hybrid chemical compounds in the sense that they possess dual functionality: they have an organic reactive group and an inorganic hydrolyzable methoxysilyl group in the same molecule. The organic group is compatible with the resins of plastics and the inorganic group bonds with and condenses on the surfaces of hydrophilic minerals. The result is strong water-resistant adhesion between the bulk resin and mineral phases through chemical bonding.

A study (1) done at ATRC in 1981 investigated one silane coupling agent, Dow Corning® Z-6020, an aminoalkyl silane, as an antistripping agent for control of debonding of asphalt and aggregate in the presence of water. Two local aggregate sources were used in the study. These aggregates differ greatly in sand equivalent (AASHTO T176) test values and, thus, in the level of naturally occurring mineral dust or filler. Testing was by immersion compression (AASHTO T165, 167) and doublepunch (TRB Record 515). These are unconfined compression and tensile tests, respectively. The results of the study indicated that addition of the coupling agent increased dry strength as well as wet strength and wet strength retention of asphalt concrete specimens. Furthermore, wet strength was seen to increase faster versus coupling agent concentration using the aggregate with the lower sand equivalent value. This led to the belief that the coupling agent was potentially a promoter of asphalt concrete strength and that this effect was enhanced if not produced through the auxiliary agency of mineral dust filler reinforcement.

ATRC made a further study (Information available upon request) of the effects of the coupling agent upon the Marshall properties of asphalt concrete using the aggregate of lower sand equivalent value from the above study. (Tables 1-3)

The coupling agent caused an increase in mixture stability at all levels of concentration at which it was applied as compared to mixtures using oven-dried aggregate without pretreatment. A study of the effects of Z-6020 and Celite (95% SiO<sub>2</sub>) upon certain properties of Edgington AR-2000 was also conducted. These results indicated a very strong influence upon asphalt rheology by Celite, although the effects of Z-6020 were unclear. (Table 4)

TABLE 1. MARSHALL TEST DATA ON OVEN-DRIED AGUA FRIA  
AGGREGATE PRETREATED WITH Z-6020

<u>Mixture</u>	<u>Sample No.</u>	<u>Density</u>	<u>Flow</u>	<u>Stability</u>
Asphalt Only	7	144.0	9	1482
" "	8	144.0	10	1483
" "	9	144.0	9	2033
" "	10	144.0	13	1942
" "	11	144.0	10	1733
" "	12	<u>142.0</u>	<u>11</u>	<u>1588</u>
Average		143.7	10	1710
Standard Deviation		0.8	1.5	235
<hr/>				
3% Additive Solution	26	142.5	9	1525
.25% by wt. of Agg.	27	142.5	11	2340
	28	<u>142.0</u>	<u>9</u>	<u>2041</u>
Average		142.33	10	1969
Standard Deviation		0.3	1.2	412
<hr/>				
3% Additive Solution	29	143.0	11	1959
.75% by wt. of Agg.	30	143.0	9	2280
	31	<u>143.0</u>	<u>8</u>	<u>2358</u>
Average		143.0	9	2199
Standard Deviation		0	1.5	211
<hr/>				
3% Additive Solution	32	141.0	13	2899
1.0% by wt. of Agg.	33	143.0	8	2330
	34	<u>143.0</u>	<u>11</u>	<u>2440</u>
Average		142.3	11	2556
Standard Deviation		1.2	2.5	302
<hr/>				
3% Additive Solution	35	144.5	13	1907.5
1.5% by wt. of Agg.	36	146.0	9	2098
	37	<u>146.5</u>	<u>11</u>	<u>2098</u>
Average		145.67	11	2035
Standard Deviation		1.0	2.0	110

TABLE 2. MARSHALL TEST DATA ON SATURATED-SURFACE-DRY  
AGUA FRIA AGGREGATE PRETREATED WITH Z-6020

<u>Mixture</u>	<u>Sample No.</u>	<u>Density</u>	<u>Flow</u>	<u>Stability</u>
1% Additive Solution	41	142.5	10	2219
0.25% by wt. of Agg.	42	142.9	11	1751
	43	<u>143.8</u>	<u>10</u>	<u>1989</u>
Average		143.1	10.3	1986
Standard Deviation		0.7	0.6	234
<hr/>				
1% Additive Solution	44	142.8	12	1768
0.75% by wt. of Agg.	45	143.1	10	1612
	46	<u>143.5</u>	<u>10</u>	<u>2041</u>
Average		143.1	10.7	1807
Standard Deviation		0.4	1.2	217
<hr/>				
1% Additive Solution	47	143.1	7	2153
1.0% by wt. of Agg.	48	143.0	14	1907
	49	<u>142.6</u>	<u>11</u>	<u>1625</u>
Average		142.9	10.7	1895
Standard Deviation		0.3	3.5	264
<hr/>				
1% Additive Solution	50	143.3	12	2142
1.5% by wt. of Agg.	51	142.3	11	1664
	52	<u>143.5</u>	<u>14</u>	<u>1830</u>
Average		143.0	12.3	1879
Standard Deviation		0.6	1.5	243
<hr/>				

TABLE 3. AGUA FRIA RIVER AGGREGATE GRADATION

<u>Sieve Size</u>	<u>Percent Passing</u>
1"	100
3/4"	94
1/2"	80
3/8"	66
#4	50
#8	45
#10	44
#16	38
#30	24
#40	17
#50	12
#100	7
#200	5

Sand Equivalent 32

TABLE 4. ASPHALT/CELITE MIXTURES

	1	2	3	<u>Composite</u>		6	7
				4	5		
Asphalt (g)	200	200	200	200	200	250	250
Celite (g)	0	20	20	10	10	50	50
Z-6020 (g)	0	1.00	0	0.50	0	1.00	0
% Celite	0	9.09	9.09	4.76	4.76	16.6	16.6
Ductility (cm), 77°F							
Original	139	78	70	97	90	64	53
RTFO Cured	145+	88	78	106	79	38	51
Absol Visc (poise), 140°F							
Original	979	1660	1700	1590	1640	9360	8450
RTFO Cured	2240	4330	4240	3830	3680	23400	23700
Index	2.28	2.61	2.49	2.41	2.24	2.50	2.80
Microvisc (poise x 10 <sup>6</sup> ), 77°F							
Original	0.967	1.55	1.33	1.57	2.41	4.70	4.82
RTFO Cured	2.35	2.80	2.76	3.24	3.40	9.18	10.4
Index	2.46	1.81	2.08	2.06	1.41	1.95	2.16
Complex Flow							
Original	0.599	0.830	0.803	0.843	0.824	0.749	0.744
RTFO Cured	0.559	0.812	0.910	0.831	0.913	0.910	0.828
Temperature Susceptibility							
Original (x10 <sup>4</sup> )	3.53	3.50	3.41	3.53	3.73	3.18	3.24
RTFO Cured (x10 <sup>4</sup> )	3.56	3.31	3.31	3.45	3.49	3.05	3.11

Dukatz and Anderson (2) investigated the mechanical effects of eight mineral fillers on asphalt and asphalt concrete mixes. Their investigations indicated tremendous stiffening effects in both binders and asphalt concrete throughout a filler concentration range in the binder from 12.5% to 50% among eight fillers as given by creep compliance measurements. They did not find significant influence on resilient modulus or Marshall stability of asphalt concrete mixtures by any of these mineral fillers. Sanderson (3) reported success in reversing the stripping tendency of hydrophillic aggregates by exposing them in a surface moist condition to a vapor phase mixture of methylchlorosilanes.

## Purpose

The primary purpose of this project was to determine whether silane-coupled asphalt/mineral composites could be made which would perform better than asphalts alone as binders in asphalt pavement. Since the work was done in the laboratory, a parallel purpose was to select suitable standard test criteria for judging and comparing composites.

Another major purpose of the project, and of this report in particular, is to explain why and how silane coupling agents can be effective in uniting asphalts and mineral fillers to form new materials which possess desirable qualities which would be unattainable without the inclusion of the coupling agent. Provisional explanations are also offered for apparent special technological requirements pertaining to asphalts and to asphalt concrete design and manufacturing. In this regard, the following three considerations may be noted:

- 1) Asphalt is not a plastic since it is not a polymeric material. It is a viscoelastic material which behaves analogously to thermoplastics in many ways.
- 2) Since asphalt has no predominant individual chemical component, the organic moiety of a silane coupler is not chosen with the specificity employed in the plastics industry. Rather, the coupling agent is selected with a view to overall compatibility with the general distribution of functionality found in asphalts.
- 3) Much attention is given in this report to the status of the asphaltenes in asphalt/mineral composites. Rostler (4) has shown how certain proportions of fractions defined by the Rostler/Sternberg analysis are required for keeping asphaltenes dispersed and that performance of an asphalt is intimately associated with its levels of asphaltenes and its ability to carry them. Guess (5) found with the scanning electron microscope that areas of brittle asphalt contained agglomerations of asphaltene micelles which were no longer peptized. The asphalt in such areas appeared highly fractured in contrast with the smooth areas of flexible asphalt where the asphaltenes were in dispersed condition. Scott (6) reported that UV-Visible and infrared spectrophotometry and number average molecular weight determination on adsorption-desorption specimens show that it is the oxygen-containing asphaltenes which predominate in the adsorbate on siliceous mineral surfaces in contact with asphalt. He believed that hydrated lime worked as an antistripping agent by removing these adsorbing components before they can form strong bonds with the mineral aggregate.

## Scope

The project was begun with a pilot study which was originally intended as an introduction to a larger program of preparation and rheological examination of composites. The pilot study composites were made with Golden Bear AR-4000 asphalt, Dow Corning Z-6020 coupling agent, and Agua Fria River -200 mesh baghouse fines. Some unexpected findings are reported and some changes in our approach to the problems of distinguishing between composites with respect to quality are described.

The next part of the project is a factorialized experiment consisting of 48 asphalt concrete test specimens in duplicate. These specimens were tested for the physical properties of Resilient Modulus, Marshall Stability, and Marshall Flow.

Finally, an investigation of asphalts, composites, minerals, and isolated asphaltene by scanning electron microscopy (SEM) was done. Several selected photomicrographs are included in this report. The emphasis placed upon asphaltene in the SEM investigation is based on the pre-eminent role ascribed to them as explained in the Purpose Section and to a fortunate facility in preparing and viewing them due to their high melting points.

The three parts of the laboratory work are, therefore:

- I. Pilot Study
- II. 96-Specimen Composite Concrete Experiment
- III. SEM Investigation

This report contains a description of the reasons for each part of the laboratory work, what was done, a presentation of the results from that part, and a discussion of the results. The report continues with an overall discussion of the project, the philosophy behind the project as a whole, certain unifying concepts relating to one or more parts of the work, and a scattering of interesting findings and theoretical considerations. The report concludes with recommendations for further research.

## PILOT STUDY

### Rationale

The pilot study was intended as an initiatory experiment using selected raw materials to open the way to a larger experiment using a wide variety of raw materials. The pilot study was supposed to help solve the problems relating to preparation, curing, handling, sampling, etc., of composite materials and making estimates in the following three areas:

- A. Needs of manpower, time, supplies, and equipment for making composites,
- B. Major trends in properties versus filler and coupler concentrations,
- C. Relative sizes of variance components:
  - 1) batch to batch
  - 2) within batch
    - a) local segregation
    - b) experimental.

It was expected that the findings for this single combination of raw materials would apply reasonably well to the other combinations to be used.

### Laboratory Work

The following raw materials were selected for making the pilot study composites:

- A. Dow Corning® Z-6020 coupling agent.
- B. Golden Bear AR-4000 base asphalt.
- C. Agua Fria River -200 mesh baghouse fines filler.

Composite specimens were made having filler concentrations in the range of 0 to 25% w/w (weight to weight) of composite and coupling agent concentrations in the range of 0 to 1.00% w/w of filler. The specimen size was 100 grams.

Specimens were made by many techniques employing various mixing conditions, temperatures, etc. The coupling agent was applied both as an integral blend in the base asphalt and as a pretreatment of the filler by various methods.

The pilot study composites were tested for the following properties (Appendix ):

- 1) Viscosity in Pascal-seconds (Pa·s) at a work rate per unit volume of 100 watt/meter<sup>3</sup> at 20°C (68 F), 30°C (86°F) before and after rolling-thin-film curing (AASHTO T240).
- 2) Shear susceptibility, C, over the shear rate interval 0.05s<sup>-1</sup> to 1.00s<sup>-1</sup> at 20°C (68°F), 30°C (86°F) before and after rolling-thin-film curing (AASHTO T240).

### Results

Tables 5-8 show some typical results from the pilot study work. The mixing was done by hand using glass stirring rods and 8 ounce seamless cans. The mixing temperature was 250°F (121°C) at the beginning when filler was poured into asphalt. Mixing was continued until cooling at room temperature prevented stirring. The coupling agent was added as a concentrate in asphalt by a dilution method to produce integral blends of the agent in base asphalt at the required concentrations.

Filler Conc. (% of Composite) Coupler Conc. (% of Filler)	0.00	5.00	10.00	15.00	20.00	25.00	RTFC (AASHTO T240)
0.00	0.741	1.05	0.680	1.44	1.86	2.19	Before
	3.34	3.52	3.15	2.80	1.92	3.15	After
	1.47	1.71	1.49	1.43	1.27	1.82	Before
0.20	3.07	2.76	1.63	2.50	2.74	3.42	After
	1.94	2.11	0.805				Before
	3.00	2.65	1.77				After
0.60			1.01				Before
			1.76				After
			0.847				Before
0.80			3.65				After
			1.59				Before
			3.28				After
1.00							

Visc. @ 100 W/m<sup>3</sup>, Pascal-seconds (x10<sup>6</sup>)  
20°C

TABLE 5. PILOT STUDY COMPOSITES

Filler Conc. (% of Composite) Coupler Conc. (% of Filler)	0.00	5.00	10.00	15.00	20.00	25.00	RTFC (AASHTO T240)
0.00	0.119	.116	0.126	0.127	0.093	.082	Before
	.104	.108	0.176	0.170	0.100	.125	After
0.20	.096	.088	0.0327	.117	.120	.125	Before
	.098	.123	0.053	.140	.122	.114	After
0.40	.100	.101	.113				Before
	.113	.125	0.158				After
0.60			0.110				Before
			0.042				After
0.80			0.145				Before
			0.247				After
1.00			0.0939				Before
			0.102				After

Visc. @ 100 W/m<sup>3</sup>, Pa.s(x10<sup>6</sup>)  
300C

TABLE 6. PILOT STUDY COMPOSITES



<div>Filler Conc. (% of Composite) Coupler Conc. (% of Filler)</div>	0.00	5.00	10.00	15.00	20.00	25.00	RTFC (AASHTO T240))
0.00	0.919	1.020	.933	.956	1.014	0.985	Before
	1.092	1.292	1.118	1.249	1.406	1.017	After
	1.113	1.284	1.322	1.252	1.101	1.001	Before
0.20	1.385	1.176	1.491	1.318	1.345	1.053	After
	0.992	1.123	1.022				Before
0.40	1.099	1.131	1.137				After
			.957				Before
0.60			1.616				After
			1.271				Before
0.80			1.011				After
			.996				Before
1.00			1.267				After

$$\text{Slope} = \frac{C}{300^\circ\text{C}}$$

## Discussion

At the very beginning of the pilot study, extreme variances were found in test results on composites at all levels of filler and coupler concentration for replicate samples and for same samples tested repeatedly. These variances were of such a magnitude as to preclude making of any claims to repeatability or reproducibility of test results. Both the filler and the coupler appeared to unpredictably raise and lower viscosities, shear susceptibilities, and temperature susceptibilities. There were no trends discernible for any property versus any independent variable.

The extreme variance in the data and the absence of verifiable improvement in composite properties over those of pure asphalt were thought to be due to poor dispersion of coupler and of filler.

To facilitate coupler dispersion when applied as an integral blend into asphalt, kerosene was used as a vehicle. Z-6020/kerosene solutions were used for coupler addition to asphalt to prevent gelling of coupler within the asphalt at localized zones of high coupler concentration. This change in mixing had little or no effect upon variance in the data. There did, however, appear to be a resulting trend toward lower viscosity with increasing coupler (and kerosene vehicle). This was probably only a thinning effect of the vehicle which was inevitable since, to maintain constant vehicular dispersion, coupler and vehicle levels can not be made independent of each other. The asphalt dilution method using a 1.00% stock solution of coupler in asphalt was employed. No improvement in data variance was made. A Waring blender was used to mix coupler and filler for better distribution of coupler as a filler pretreatment. The problems persisted.

Asphalts and filler specimens were mixed under very high shear conditions using Jiffy mixers at 2500 rpm, sampled quickly, and tested. No improvement in data variance was observed and no trends were uncovered.

## 96-SPECIMEN COMPOSITE CONCRETE EXPERIMENT

### Rationale

Because of the problems described, the planned larger experiment was abandoned and a combined asphalt concrete/composite testing program started in which the asphalt concrete specimens differed only in binder types. The binders used were to be asphalt/mineral composites with silane coupling agents. The objective was to find how to make silane-coupled asphalt/mineral composite materials with superior qualities relative to pure asphalts. The composites were to be compared as variable components of asphalt concrete rather than as separate entities. The properties thus measured promised to be more meaningful and relevant to paving construction, and hopefully, more indicative of composite quality.

A factorialized experiment with a randomized test sequence was used (Table 9) for a condensed analysis of the effects of all of the above factors. This experiment would also yield information about some interactions among various independent variables. The variables and constants are listed in Table 10.

The two asphalts, Golden Bear and Huntway, were chosen because of their disparate properties. These represented two widely different values of several properties tested for in asphalts. The two fillers, Agua Fria and Salt River baghouse fines, were chosen because they were inexpensive and plentiful. Table 11 lists properties of these raw materials. The base aggregate gradation is shown in Table 12. The five constants listed in Table 10 were maintained to determine how the levels of the independent variables affected values of the dependent variables listed in the same table.

A disadvantage to the experiment was in the way the binder was produced: in situ, not as a separate prefabricated component; the mixing step used to make the asphalt concrete specimens was also used to create within the mixes an asphalt/mineral phase to represent a composite binder.

ASPHALT TYPE A<sub>i</sub>  
 COUPLER APPLICATION METHOD B<sub>j</sub>  
 COUPLER CONCENTRATION (BASED ON AGGREGATE), C<sub>k</sub>  
 FILLER CONCENTRATION D<sub>l</sub>  
 FILLER TYPE E<sub>m</sub>

			AGUA FRIA		SALT RIVER	
			4.0%	8.0%	4.0%	8.0%
GOLDEN BEAR	ASPHALT BLEND	0%	48	83	94	27
			49	84	1	43
		0.05%	95	85	40	86
			96	3	41	18
		0.10%	51	6	73	33
			7	71	81	79
	PRETREATED AGGREGATE	0%	8	72	82	80
			88	92	64	42
		0.05%	91	93	65	4
			30	5	68	21
		0.10%	10	13	55	22
			60	20	57	37
HUNTWAY	ASPHALT BLEND	0%	78	15	58	38
			36	16	69	63
		0.05%	29	17	70	28
			39	2	25	31
		0.10%	74	11	26	32
			75	12	54	47
	PRETREATED AGGREGATE	0%	46	44	56	52
			61	50	59	53
		0.05%	62	45	19	76
			89	66	34	77
		0.10%	90	67	35	24
			14	9	23	87

TABLE 9.

96-SPECIMEN  
 EXPERIMENT  
 RANDOM TEST  
 SEQUENCE

RANDOMIZED-TEST MATRIX

TABLE 10

ELEMENTS OF 96-SPECIMEN EXPERIMENTINDEPENDENT VARIABLES

1. Asphalt Type,  $A_i$   
i = 1, Golden Bear (Valley)  
i = 2, Huntway (Coastal)
2. Coupler Application Method,  $B_j$   
j = 1, Asphalt Blend  
j = 2, Pretreated Aggregate (soaked)
3. Coupler Concentration (based on aggregate),  $C_k$   
k = 1, 0%  
k = 2, 0.05%  
k = 3, 0.10%
4. Filler Concentration,  $D_l$   
l = 1, 4.0%  
l = 2, 8.0%
5. Filler Type,  $E_m$   
m = 1, Agua Fria - 200 mesh baghouse  
m = 2, Salt River - 200 mesh baghouse

DEPENDENT VARIABLES

1. Modulus of Resilience
2. Marshall Stability
3. Marshall Flow

CONSTANTS

1. Asphalt Concentration (5%)
2. Coupler Type (Z-6020)
3. Aggregate Source and Gradation (Salt River)
4. Mixing Conditions (Marshall)
5. Compaction (Marshall)

TABLE 11

PROPERTIES OF ASPHALTS AND BAGHOUSE FILLERS

Asphalts:	Golden Bear AR-4000	Huntway AR-4000
Arizona 509		
Modified Rostler-Sternberg, per cent		
Asphaltenes	9.35	22.89
N+A <sub>1</sub>	54.63	44.42
A <sub>2</sub> +P	36.02	32.69
CRR	1.52	1.36
Kinematic Viscosity		
AASHTO T201, centistokes		
Before RTFC	277.4	292.3
After RTFC	344.6	501.9
Ratio (Aging Index)	1.24	1.72
Fillers:	Agua Fria	Salt River
	-200 baghouse	-200 baghouse
Bulk Density, g/cc	1.15	0.89
Bulk Volume, cc/g	0.87	1.12
Specific Gravity		
AASHTO T100	2.74	2.73

TABLE 12

SALT RIVER AGGREGATE GRADATION

<u>Sieve</u>	<u>% Retained</u>	<u>% Passing</u>
1"		100
3/4"	2	98
1/2"	10	88
3/8"	15	73
1/4"	14	59
#4	6	53
#8	10	43
#10	3	40
#16	7	33
#30	10	23
#40	4	19
#50	5	14
#100	7	7
#200	4	3

## Laboratory Work

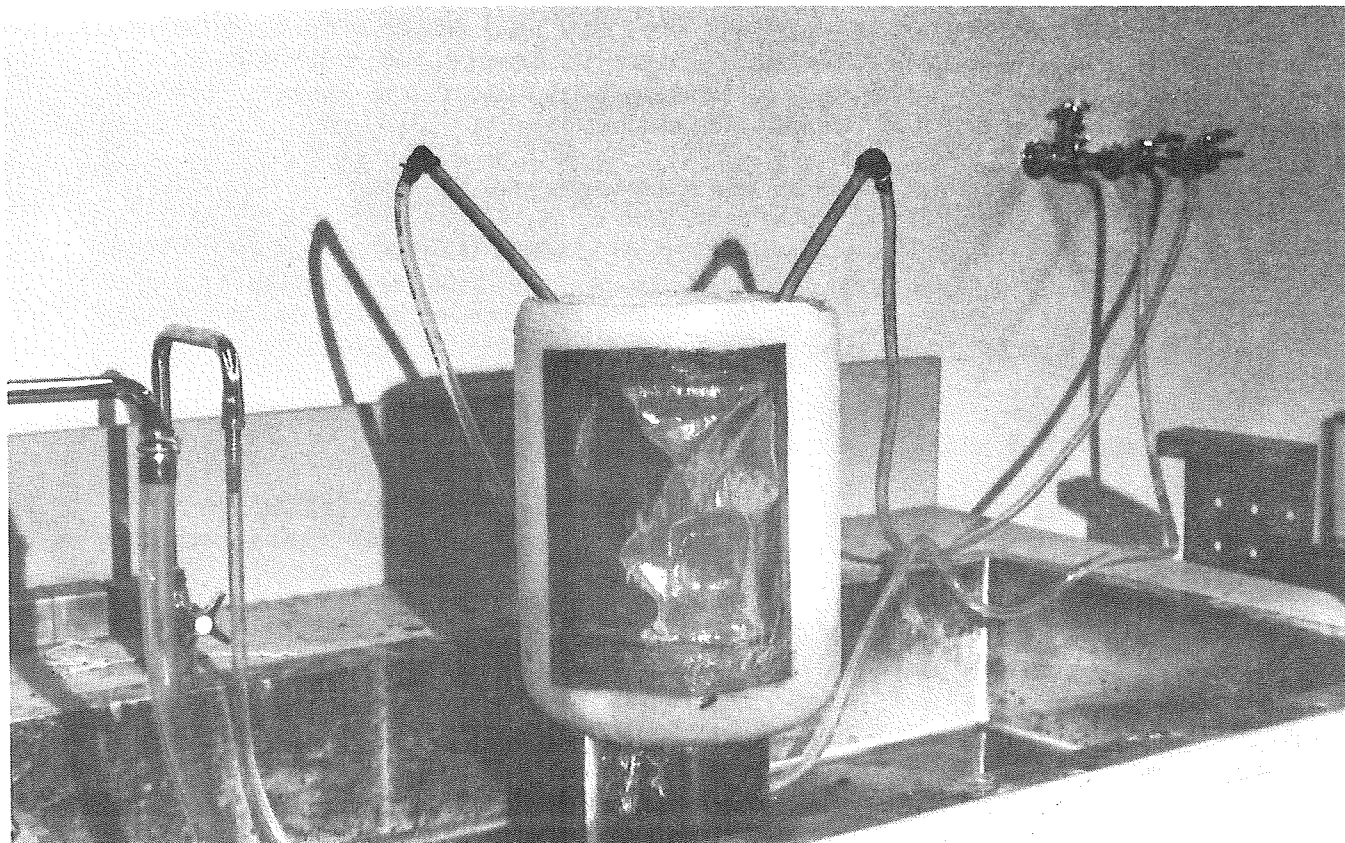
A factorialized experiment was established that contained 48 asphalt concrete test specimens in duplicate (Table 9). The specimens were manufactured by the Asphalt Institute Marshall mix design method (7). One thousand pounds of Salt River aggregate (Table 12) was washed free of -200 mesh fines in special elutriation bottles made in our laboratory (Figure 1); then it was separated into 13 sizes and stockpiled for the experiment. Large stocks of the two mineral fillers, Agua Fria and Salt River -200 mesh baghouse fines, were sieved and set aside to be used as levels for the independent variable "filler type". The two asphalts, Golden Bear and Huntway AR4000, were likewise stockpiled for "asphalt types".

The two coupler application methods were as follows:

1. Pretreated Aggregate - A solution of Z-6020 in 500 ml of distilled water was prepared and used to immerse the 1100g aggregate fraction for each specimen. The aggregate and coupler solution in the mixing pan was placed in an oven to dry overnight at 105°C (221°F).
2. Asphalt Blends - Aliquots of a 1% solution of Z-6020 in asphalt were blended into asphalt diluent at 121°C (250°F).

The properties originally chosen for the dependent variables in the experiment were tensile strength, instantaneous tensile stiffness modulus (E-Modulus) and failure strain. A copy of the tensile displacement device described by Lottman (8) was fabricated. These properties and this instrument were selected because they emphasize the influence of binder properties such as adhesion, cohesion, and rheology, and de-emphasize aggregate properties. (The procedures used in (1), immersion compression and double punch, are unconfined compression and indirect tensile type tests which also emphasize binder effects).

Unfortunately, the specimens exhibited tensile strength values too low to adequately compare specimens. Also, the specimens failed too early at the minimum deformation rate to allow for plotting a sufficient number of tensile stiffness modulus versus time data points to obtain E-Modulus values. Resilient modulus was measured with a Retsina Mark IV resilient modulus apparatus. As this was a nondestructive test, Marshall tests (stability, flow, and density) were also run.



**Fig. 1.**

**Elutriation Bottle with 200 Mesh Fabric Windows**

## Results

As shown in Table 9, there were three concentrations of coupler based upon weight of aggregate and two concentrations of filler based upon weight of specimen. The variables and constants are listed in Table 10. As noted, this experiment does not utilize silane-coupled asphalt/mineral composites as binders in the asphalt concrete. The mineral filler is added to the mix as part of the aggregate and the asphalt with and without coupler ( $j = 1$  and  $j = 2$ ) is added to the mix as in standard Marshall methodology. There is no prefabrication of composite binders.

The testing was carried out in randomized sequence on all 96 specimens and the test data processed by three procedures using the Statistical Analysis System (SAS):

1. Analysis of Variance
2. General Linear Models
3. Stepwise

The results of the modulus of resilience, Marshall stability, and Marshall flow testing are shown in Tables 13, 14, and 15 respectively. The statistical analyses for modulus of resilience are presented in Tables 16a-e. The complete analysis of variance table is included as Table 16a. This includes all interactions among independent variables A, B, C, D, E up to and including fifth order  $A*B*C*D*E$ . The means are listed in Tables 16b-d. The SAS Stepwise Table is reproduced up to the best three-variable model in Table 16e.

## Discussion

At a confidence level of 99%, it is seen in Table 16a that all of the single variables except D (filler concentration) have significant effects upon modulus of resilience. ( $M_R$ ) The fact that all variables except one are significant here is an indication of the sensitivity of this property to the independent variables. As higher values for  $M_R$  are indicative of superior performance, the mean values of  $M_R$  at the levels of each independent variable were examined. (Table 16b)

Asphalt Type A<sub>1</sub> (Golden Bear) produces a mean resilience approximately two-fold greater than that for A<sub>2</sub> (Huntway). This is an important discovery when viewed in connection with the chemical differences known to exist between these asphalts. It is further physical evidence of underlying divergences in chemical properties. Golden Bear asphalt is much higher in basic nitrogen compounds. It is, in fact, an alkaline material and can be shown to impart a pH of 9 - 10 to ten times its own volume of neutral water upon gentle heating. Huntway asphalt is, like most other asphalts, an acidic material. Huntway has nearly two-and-one-half times as much asphaltenes by weight as Golden Bear.

The means for B (coupler application method) indicate greater resilience where the coupler was applied as an aggregate pretreatment, i.e., B<sub>2</sub>. The combination means for A and B show this difference to occur with both asphalts. By depositing the coupler directly onto the aggregate before

ASPHALT TYPE A<sub>i</sub>  
 COUPLER APPLICATION METHOD B<sub>j</sub>  
 COUPLER CONCENTRATION (BASED ON AGGREGATE), C<sub>k</sub>  
 FILLER CONCENTRATION D<sub>l</sub>  
 FILLER TYPE E<sub>m</sub>

TABLE 13  
 MODULUS OF  
 RESILIENCE  
 (psi x 1000)

			AGUA FRIA		SALT RIVER	
			4.0%	8.0%	4.0%	8.0%
GOLDEN BEAR	ASPHALT BLEND	0%	527	696	511	776
			936	901	506	626
		0.05%	323	412	307	472
			371	357	254	475
		0.10%	376	384	435	388
			244	341	329	385
	PRETREATED AGGREGATE	0%	579	888	641	643
			430	543	611	719
		0.05%	397	464	628	594
			460	899	660	353
		0.10%	585	381	631	389
			658	377	670	650
HUNTWAY	ASPHALT BLEND	0%	216	222	257	251
			168	207	263	226
		0.05%	170	322	303	332
			212	279	182	274
		0.10%	263	324	216	301
			251	300	274	318
	PRETREATED AGGREGATE	0%	169	254	233	456
			279	266	294	285
		0.05%	190	291	186	301
			229	247	155	302
		0.10%	220	310	192	715
			202	233	165	335

RANDOMIZED-TEST MATRIX

TABLE 14  
MARSHALL  
STABILITY  
(LBS)

				AGUA FRIA		SALT RIVER	
				4.0%	8.0%	4.0%	8.0%
GOLDEN BEAR	ASPHALT BLEND	0%		2425	2132	2054	2978
				2202	2875	2080	2574
		0.05%		1859	2398	1508	1677
				1751	2836	1573	2166
		0.10%		2245	2548	1730	2750
				1889	2475	2139	2235
	PRETREATED AGGREGATE	0%		2017	2548	2902	2507
				2201	2834	1733	2223
		0.05%		2054	3066	1283	2822
				1733	2651	2132	2453
		0.10%		2235	2651	1846	2266
				1859	2736	1989	2278
HUNTWAY	ASPHALT BLEND	0%		1959	2998	1785	2603
				1959	2872	1998	2115
		0.05%		1575	2834	2271	2245
				1456	3173	2522	2420
		0.10%		1785	2834	2507	2519
				2289	3147	2080	2307
	PRETREATED AGGREGATE	0%		1677	2236	1588	2630
				2210	2861	1560	2822
		0.05%		2041	2362	2053	2534
				1989	2509	2166	2679
		0.10%		1989	2198	2163	2245
				1989	3078	1729	2139

RANDOMIZED-TEST MATRIX

ASPHALT TYPE A<sub>i</sub>

COUPLER APPLICATION METHOD B<sub>j</sub>

COUPLER CONCENTRATION (BASED ON AGGREGATE), C<sub>k</sub>

FILLER CONCENTRATION D<sub>l</sub>

FILLER TYPE E<sub>m</sub>

TABLE 15

MARSHALL  
FLOW  
(0.01 INCH)

			AGUA FRIA		SALT RIVER	
			4.0%	8.0%	4.0%	8.0%
GOLDEN BEAR	ASPHALT BLEND	0%	14	10	10	16
			10	10	9	16
		0.05%	11	9	11	12
			8	7	12	12
		0.10%	11	13	7	11
			10	12	9	13
	PRETREATED AGGREGATE	0%	9	12	12	16
			10	10	12	14
		0.05%	13	13	12	13
			11	14	11	14.5
		0.10%	8	10	11	11
			9	13	12	12
HUNTWAY	ASPHALT BLEND	0%	10	12	13	14
			10	15	10	12
		0.05%	12.5	11	13	10
			10	10.5	15	13
		0.10%	10	8	9	14
			9	11	10	12
	PRETREATED AGGREGATE	0%	12	11	15	13
			10	12	9	14
		0.05%	9	12	10	14
			11	11	10	13
		0.10%	12	11	10	15
			14	10	10	12

RANDOMIZED-TEST MATRIX

TABLE 16a. 96-SPEC ANALYSIS OF VARIANCE PROCEDURE

DEPENDENT VARIABLE: Y = MODULUS OF RESILIENCE												
SOURCE	DF	SUM OF SQUARES	ANOVA SS	F VALUE	PR > F	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	PR > F	STD DEV	C.V.
MODEL	47	2976959.95833333				63339.57358156	6.23	0.0001	0.859177			25.5910
ERROR	48	487936.00000000				10165.33333333						Y MEAN
CORRECTED TOTAL	95	3464895.95833333								100.82327774		393.97916667
SOURCE	DF	ANOVA SS	F VALUE	PR > F	R-SQUARE	PR > F	STD DEV	C.V.	Y MEAN			
A	1	1638560.04166667	161.19	0.0001	0.0001	0.0001						
B	1	87362.66666667	8.59	0.0052	0.0052	0.0052						
C	2	185263.89583333	9.11	0.0004	0.0004	0.0004						
D	1	12973.50000000	1.28	0.2642	0.2642	0.2642						
E	1	100492.04166667	9.89	0.0029	0.0029	0.0029						
A*B	1	47704.16666666	4.69	0.0353	0.0353	0.0353						
A*C	2	260545.77083333	12.82	0.0001	0.0001	0.0001						
A*D	1	7848.16666667	0.77	0.3840	0.3840	0.3840						
A*E	1	10795.04166667	1.06	0.3079	0.3079	0.3079						
B*C	2	44755.39583333	2.20	0.1217	0.1217	0.1217						
B*D	1	20358.37500000	2.00	0.1635	0.1635	0.1635						
B*E	1	620.16666666	0.06	0.8060	0.8060	0.8060						
C*D	2	15634.31250000	0.77	0.4691	0.4691	0.4691						
C*E	2	17749.52083333	0.87	0.4242	0.4242	0.4242						
D*E	1	504.16666667	0.05	0.8247	0.8247	0.8247						
A*B*C	2	116339.77083334	5.72	0.0059	0.0059	0.0059						
A*B*D	1	2262.04166667	0.22	0.6393	0.6393	0.6393						
A*B*E	1	43520.16666667	4.28	0.0439	0.0439	0.0439						
A*C*D	2	20887.77083333	1.03	0.3657	0.3657	0.3657						
A*C*E	2	96510.89583333	4.75	0.0131	0.0131	0.0131						
A*D*E	1	14016.66666667	1.38	0.2461	0.2461	0.2461						
B*C*D	2	19375.56250000	0.95	0.3927	0.3927	0.3927						
B*C*E	2	6724.52083334	0.33	0.7200	0.7200	0.7200						
B*D*E	1	1488.37500000	0.15	0.7037	0.7037	0.7037						
C*D*E	2	23141.27083333	1.14	0.3289	0.3289	0.3289						
A*B*C*D	2	16546.02083333	0.81	0.4492	0.4492	0.4492						
A*B*C*E	2	26764.39583333	1.32	0.2776	0.2776	0.2776						
A*B*D*E	1	61307.04166666	6.03	0.0177	0.0177	0.0177						
A*C*D*E	2	3673.39583333	0.18	0.8353	0.8353	0.8353						
B*C*D*E	2	52016.68750000	2.56	0.0879	0.0879	0.0879						
A*B*C*D*E	2	21218.14583334	1.04	0.3600	0.3600	0.3600						

TABLE 16b. 96-SPEC ANALYSIS OF VARIANCE PROCEDURE (MEANS)

A	N	Y	A	D	N	Y	C	E	N	Y		
1	48	524.625000	1	1	24	522.041667	1	1	16	413.750000		
2	48	263.333333	1	2	24	527.208333	1	2	16	497.437500		
			2	1	24	242.666667	2	1	16	314.187500		
B	N	Y	2	2	24	284.000000	2	2	16	398.375000		
1	48	363.812500					3	1	16	356.937500		
2	48	424.145833	A	E	N	Y	3	2	16	383.187500		
			1	1	24	502.875000						
C	N	Y	1	2	24	546.375000	D	E	N	Y		
1	32	455.593750	2	1	24	220.375000	1	1	24	352.291667		
2	32	356.281250	2	2	24	306.291667	1	2	24	412.416667		
3	32	370.062500					2	1	24	370.958333		
			B	C	N	Y	2	2	24	440.250000		
D	N	Y	1	1	16	455.562500	A	B	C	N	Y	
1	48	382.354167	1	2	16	315.312500	1	1	1	8	684.875000	
2	48	405.604167	1	3	16	320.562500	1	1	2	8	371.375000	
			2	1	16	455.625000	1	1	3	8	360.250000	
E	N	Y	2	2	16	397.250000	1	2	1	8	631.750000	
1	48	361.625000	2	3	16	419.562500	1	2	2	8	556.875000	
2	48	426.333333					1	2	3	8	542.625000	
			B	D	N	Y	2	1	1	8	226.250000	
A	B	N	Y	1	1	24	366.750000	2	1	2	8	259.250000
1	1	24	472.166667	1	2	24	360.875000	2	1	3	8	280.875000
1	2	24	577.083333	2	1	24	397.958333	2	2	1	8	279.500000
2	1	24	255.458333	2	2	24	450.333333	2	2	2	8	237.625000
2	2	24	271.208333					2	2	3	8	296.500000
			B	E	N	Y						
A	C	N	Y	1	1	24	328.916667	A	B	D	N	Y
1	1	16	658.312500	1	2	24	398.708333	1	1	1	12	489.000000
1	2	16	464.125000	2	1	24	394.333333	1	1	2	12	455.333333
1	3	16	451.437500	2	2	24	453.958333	1	2	1	12	555.083333
2	1	16	252.875000					1	2	2	12	599.083333
2	2	16	248.437500	C	D	N	Y	2	1	1	12	244.500000
2	3	16	288.687500	1	1	16	455.062500	2	1	2	12	266.416667
				1	2	16	456.125000	2	2	1	12	240.833333
				2	1	16	351.437500	2	2	2	12	301.583333
				2	2	16	361.125000					
				3	1	16	340.562500	A	B	E	N	Y
				3	2	16	399.562500	1	1	1	12	426.583333
								1	1	2	12	517.750000
								1	2	1	12	579.166667
								1	2	2	12	575.000000
								2	1	1	12	231.250000
								2	1	2	12	279.666667

TABLE 16c. 96-SPEC ANALYSIS OF VARIANCE PROCEDURE (MEANS)

A	B	E	N	Y	B	C	D	N	Y	C	D	E	N	Y	
2	2	1	12	209.500000	1	1	1	8	484.125000	3	1	1	8	349.875000	
2	2	2	12	332.916667	1	1	2	8	427.000000	3	1	2	8	331.250000	
A	C	D	N	Y	1	2	1	8	305.750000	3	2	1	8	364.000000	
1	1	1	8	687.500000	1	2	2	8	324.875000	3	2	2	8	435.125000	
1	1	2	8	629.125000	1	3	1	8	310.375000	A	B	C	D	N	Y
1	2	1	8	460.375000	1	3	2	8	330.750000	1	1	1	1	4	765.000000
1	2	2	8	467.875000	2	1	1	8	426.000000	1	1	1	2	4	604.750000
1	3	1	8	418.250000	2	1	2	8	485.250000	1	1	2	1	4	365.750000
1	3	2	8	484.625000	2	2	1	8	397.125000	1	1	2	2	4	377.000000
2	1	1	8	222.625000	2	2	2	8	397.375000	1	1	2	1	4	336.250000
2	1	2	8	283.125000	2	3	1	8	370.750000	1	1	3	1	4	336.250000
2	2	1	8	242.500000	2	3	2	8	468.375000	1	1	3	2	4	384.250000
2	2	2	8	254.375000	B	C	E	N	Y	1	2	1	1	4	610.000000
2	3	1	8	262.875000	1	1	1	8	423.000000	1	2	1	2	4	653.500000
2	3	2	8	314.500000	1	1	2	8	488.125000	1	2	2	1	4	555.000000
A	C	E	N	Y	1	2	1	8	265.250000	1	2	2	2	4	558.750000
1	1	1	8	592.625000	1	2	2	8	365.375000	1	2	3	1	4	500.250000
1	1	2	8	724.000000	1	3	1	8	298.500000	1	2	3	2	4	585.000000
1	2	1	8	425.000000	1	3	2	8	342.625000	2	1	1	1	4	203.250000
1	2	2	8	503.250000	2	1	1	8	404.500000	2	1	1	2	4	249.250000
1	3	1	8	491.000000	2	1	2	8	506.750000	2	1	2	1	4	245.750000
1	3	2	8	411.875000	5	2	1	8	363.125000	2	1	2	2	4	272.750000
2	1	1	8	234.875000	2	2	2	8	431.375000	2	1	3	1	4	284.500000
2	1	2	8	270.875000	2	3	1	8	415.375000	2	1	3	2	4	277.250000
2	2	1	8	203.375000	2	3	2	8	423.750000	2	2	1	1	4	242.000000
2	2	2	8	293.500000	B	D	E	N	Y	2	2	1	2	4	317.000000
2	3	1	8	222.875000	1	1	1	12	338.083333	2	2	2	1	4	239.250000
2	3	2	8	354.500000	1	1	2	12	395.416667	2	1	1	2	4	236.000000
A	D	E	N	Y	1	2	1	12	319.750000	2	2	3	1	4	241.250000
1	1	1	12	490.500000	1	2	2	12	402.000000	2	2	3	2	4	351.750000
1	1	2	12	553.583333	2	1	1	12	366.500000	A	B	C	E	N	Y
1	2	1	12	515.250000	2	1	2	12	429.416667	1	1	1	1	4	620.000000
1	2	2	12	539.166667	2	2	1	12	422.166667	1	1	1	2	4	749.750000
2	1	1	12	214.083333	2	2	2	12	478.500000	1	1	2	1	4	313.750000
2	1	2	12	271.250000	C	D	E	N	Y	1	1	2	2	4	429.000000
2	2	1	12	226.666667	1	1	1	8	413.000000	1	1	3	1	4	346.000000
2	2	2	12	341.333333	1	1	2	8	497.125000	1	1	3	2	4	374.500000
					1	2	1	8	414.500000	1	2	1	1	4	565.250000
					1	2	2	8	497.750000	1	2	1	2	4	698.250000
					2	1	1	8	294.000000	1	2	2	1	4	536.250000
					2	1	2	8	408.875000	1	2	2	2	4	577.500000
					2	2	1	8	334.375000	1	2	3	1	4	636.000000
					2	2	2	8	387.875000	1	2	3	2	4	449.250000
										2	1	1	1	4	226.000000
										2	1	1	2	4	226.500000
										2	1	2	1	4	216.750000
										2	1	2	2	4	301.750000

TABLE 16d. 96-SPEC ANALYSIS OF VARIANCE PROCEDURE (MEANS)

A	B	C	E	N	Y	A	C	D	E	N	Y	A	B	C	D	E	N	Y	
2	1	3	1	4	251.000000	2	3	1	1	4	234.000000	1	2	2	1	1	2	428.500000	
2	1	3	2	4	310.750000	2	3	1	2	4	291.750000	1	2	2	1	2	2	681.500000	
2	2	1	1	4	243.750000	2	3	2	1	4	211.750000	1	2	2	2	1	2	644.000000	
2	2	1	2	4	315.250000	2	3	2	2	4	417.250000	1	2	2	2	2	2	473.500000	
2	2	2	1	4	190.000000							1	2	3	1	1	2	621.500000	
2	2	2	2	4	285.250000	B	C	D	E	N	Y	1	2	3	1	2	2	379.000000	
2	2	3	1	4	194.750000	1	1	1	1	4	461.750000	1	2	3	2	1	2	650.500000	
2	2	3	2	4	398.250000	1	1	1	2	4	506.500000	1	2	3	2	2	2	519.500000	
A	B	D	E	N	Y	1	1	2	1	4	384.250000	2	1	1	1	1	2	192.000000	
1	1	1	1	6	462.833333	1	1	2	2	4	469.750000	2	1	1	1	2	2	214.500000	
1	1	1	2	6	515.166667	1	2	1	1	4	269.000000	2	1	1	2	1	2	260.000000	
1	1	2	1	6	390.333333	1	2	1	2	4	342.500000	2	1	1	2	2	2	238.500000	
1	1	2	2	6	520.333333	1	2	2	1	4	261.500000	2	1	2	1	1	2	191.000000	
1	2	1	1	6	518.166667	1	2	2	2	4	388.250000	2	1	2	1	2	2	300.500000	
1	2	1	2	6	592.000000	1	3	1	1	4	283.500000	2	1	2	2	1	2	242.500000	
1	2	2	1	6	640.166667	1	3	1	2	4	337.250000	2	1	2	2	2	2	303.000000	
1	2	2	2	6	558.000000	1	3	2	1	4	313.500000	2	1	3	1	1	2	257.000000	
2	1	1	1	6	213.333333	1	3	2	2	4	348.000000	2	1	3	1	1	2	312.000000	
2	1	1	2	6	275.666667	2	1	1	1	4	364.250000	2	1	3	2	1	2	245.000000	
2	1	2	1	6	249.166667	2	1	1	2	4	487.750000	2	1	3	2	2	2	309.500000	
2	1	2	2	6	283.666667	2	1	2	1	4	444.750000	2	2	1	1	1	2	224.000000	
2	2	1	1	6	214.833333	2	1	2	2	4	525.750000	2	2	1	1	2	2	260.000000	
2	2	1	2	6	266.833333	2	2	1	1	4	319.000000	2	2	1	2	1	2	263.500000	
2	2	2	1	6	204.166667	2	2	1	2	4	475.250000	2	2	1	2	2	2	370.500000	
2	2	2	2	6	399.000000	2	2	2	1	4	407.250000	2	2	2	1	1	2	209.500000	
A	C	D	E	N	Y	2	2	2	2	4	387.500000	2	2	2	1	2	2	269.000000	
1	1	1	1	3	618.000000	2	2	2	2	4	416.250000	2	2	2	2	1	2	170.500000	
1	1	1	2	4	757.000000	2	3	1	1	4	325.250000	2	2	2	2	2	2	301.500000	
1	1	2	1	4	567.250000	2	3	1	2	4	414.500000	2	2	3	1	1	2	211.000000	
1	1	2	2	4	691.000000	2	3	2	1	4	522.250000	2	2	3	1	2	2	271.500000	
1	2	1	1	4	387.750000	A	B	C	D	E	N	Y	2	2	3	2	1	2	178.500000
1	2	1	2	4	533.000000	1	1	1	1	1	2	731.500000	2	2	3	2	2	2	525.000000
1	2	2	1	4	462.250000	1	1	1	1	2	2	798.500000							
1	2	2	2	4	473.500000	1	1	1	2	1	2	508.500000							
1	3	1	1	4	465.750000	1	1	1	2	2	2	701.000000							
1	3	1	2	4	370.750000	1	1	2	1	1	2	347.000000							
1	3	2	1	4	516.250000	1	1	2	1	2	2	384.500000							
1	3	2	2	4	453.000000	1	1	2	2	1	2	280.500000							
2	1	1	1	4	208.000000	1	1	2	2	2	2	473.500000							
2	1	1	2	4	237.250000	1	1	3	1	1	2	310.000000							
2	1	2	1	4	261.750000	1	1	3	1	2	2	362.500000							
2	1	2	2	4	304.500000	1	1	3	2	1	2	382.000000							
2	2	1	1	4	200.250000	1	2	1	1	1	2	504.500000							
2	2	1	2	4	284.750000	1	2	1	1	2	2	715.500000							
2	2	2	1	4	206.500000	1	2	1	2	1	2	626.000000							
2	2	2	2	4	302.250000	1	2	1	2	2	2	681.000000							

TABLE 16e. 96-SPEC STEPWISE EXAMPLE MAXIMUM R-SQUARE IMPROVEMENT FOR DEPENDENT VARIABLE Y

STEP 1 VARIABLE A ENTERED		R SQUARE = 0.47290310		C(P) = 16.96571963	
	DF	SUM OF SQUARES	MEAN SQUARE	F	PRPB>F
REGRESSION	1	1638560.04166667	1638560.04166667	84.34	0.0001
ERROR	94	1826335.91666667	19429.10549645		
TOTAL	95	3464895.95833333			
B VALUE		STD ERROR	TYPE II SS	F	PROB>F
INTERCEPT	785.91666667				
A	-261.29166667	28.45252295	1638560.04166667	84.34	0.0001
THE ABOVE MODEL IS THE BEST 1 VARIABLE MODEL FOUND.					
STEP 2 VARIABLE C ENTERED		R SQUARE = 0.50668464		C(P) = 11.98212774	
	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB>F
REGRESSION	2	1755609.55729167	877804.77864583	47.76	0.0001
ERROR	93	1709286.40104167	18379.42366711		
TOTAL	95	3464895.95833333			
B VALUE		STD ERROR	TYPE II SS	F	PROB>F
INTERCEPT	871.44791667				
A	-261.29166667	27.67326001	1638560.04166667	89.15	0.0001
C	-42,76562500	16.94634163	117049.51562500	6.37	0.0133
THE ABOVE MODEL IS THE BEST 2 VARIABLE MODEL FOUND.					
STEP 3 VARIABLE E ENTERED		R SQUARE = 0.53568754		C(P) = 7.98641384	
	DF	SUM OF SQUARES	MEAN SQUARE	F	PROB>F
REGRESSION	3	1856101.59895833	618700.53298611	35.38	0.0001
ERROR	92	1608794.35937500	17486.89521060		
TOTAL	95	3464895.95833333			
B VALUE		STD ERROR	TYPE II SS	F	PROB>F
INTERCEPT	774.38541667				
A	-261.29166667	26.99297379	1638560.04166667	93.70	0.0001
C	-42.76562500	16.52975310	117049.51562500	6.69	0.0112
E	64.70833333	26.99297379	100492.04166667	5.75	0.0185
THE ABOVE MODEL IS THE BEST 3 VARIABLE MODEL FOUND.					

introduction of asphalt, more efficient use of coupler is expected. The coupler is completely hydrolyzed and fixed on the mineral surface. There is no dependence upon migration of coupler through the asphalt to accumulate at the asphalt/filler (or asphalt/aggregate) interfaces. The mixing time was probably too short for the very small coupler concentration gradients within blends to completely transfer coupler to the filler. Also, some of the coupler may be denatured or consumed by reaction with asphalt components before reaching the filler surfaces when coupler is applied as an integral blend in asphalt.

There is a downward trend in resilience with increasing coupler using Golden Bear asphalt; the trend is sharper in blends than in pretreated aggregates. There is an upward trend with Huntway. As can be seen in the means for coupler concentration C, the trend with Golden Bear overrides that for Huntway. Some facts about aminoorganofunctional silanes such as Z-6020 (N-(beta-aminoethyl)-gamma-aminopropyltrimetoxysilane) as coupling agents have recently come to our attention which explain this difference in performance with these two asphalts.

Plueddemann (9, 10, 11) is credited with elucidating the mechanism by which a silane coupling agent improves the bonding situation at the interface of a composite material. Contrary to earlier opinion, his theory shows how not strong but relatively weak bonding is the source of silane couplers' advantage. Whether the silane coupler is a trichloro - or trialkoxy - organofunctional silane, it must first be hydrolyzed (in the presence of water) to an organo-functional silanol form. This derivative silanol form of the coupler then is competitive with water itself for the hydrophilic mineral surface. (It should be noted that all metallic, silicic, and aluminous oxide surfaces will be hydroxylated and hydrated and that water is ever-present even at moderately high temperatures. This is why couplers can function as integral blends in asphalt, plastic resins, etc.) The silanol diffuses over the water-covered mineral surface and, like water, forms reversible hydrogen bonds with the hydroxylated surface. But, unlike water, the silanol has organic functionality which draws the asphalt into close association with the mineral surface. Now the critical difference in the bonding situation here is that water is not detrimental, but essential. Hydrogen bonds are formed between silanols and hydroxyl compounds in the mineral surface with the elimination of water of hydration. Conversely, addition of water can easily break these bonds. Under proper conditions, these bonds represent the final means of adhesion between phases. Their low activation energy and instability to the action of water enables them to be formed, broken, reformed, etc. They can blithely reform between original molecular partners or shift and reform with new partners at adjacent positions when the bulk material is subjected to deformational stresses. Even protracted exposure to boiling water will not cause loss of adhesion. The practically infinite number of these bonds per unit area ensures a constant plenary adhesion between organic and inorganic components. Plueddemann (9) states ". . . silane coupling agents provide a bond at the interface that is capable of using the hydrolytic intrusion of water, with self-healing, as a means of stress relaxation without disrupting the overall bond between plastic and mineral surface."

Silane coupling agents can replace the undesirable strong bonds between asphaltene molecules and mineral surface groups. But in so doing, they instate their own bonding which confers the advantages described above. It

should be noted in this regard that the modulus of resilience data show Golden Bear asphalt, with its much lower concentration of asphaltenes, to yield much greater resilience. This may be largely attributable to the capacity of Golden Bear maltenes to support asphaltenes-preventing their deposition onto the mineral surface. Also, it may be due to the simple underabundance of asphaltenes in this asphalt.

It has recently been reported by plastics industry technologists that cationic organofunctional silane coupling agents are less effective in their free amine form than they are in their cationic form. An alkaline medium would render the free amine. Lotz (12) found that alkaline conditions actually caused a lowering of strength through aminefunctional silanes in epoxy-anhydride resins with glass reinforcement. The trend in resilience versus coupler appearing with Golden Bear asphalt may be attributable to the alkaline condition present in this asphalt.

It will be seen that the filler of higher bulk volume, Salt River, imparts a higher modulus of resilience to specimens than does Agua Fria. Also, the higher concentration of filler of each type imparts a higher value. This may indicate that the bulk volume of a filler is a relevant property and that phase volume ratios should be considered useful in composite binder manufacturing.

Another matter concerning the bulk acid-base character of asphalts is the effects of this character upon the surfaces of mineral particles. As noted earlier, metal oxides, silicates, aluminates, etc., have hydrated hydroxyl groups at their surfaces. A pH-dependent surface potential, called zeta potential, is present at the surface. There will be a certain pH value at which the zeta potential changes from positive to negative and the surface will change from cationic to anionic. The pH at which change occurs is called the isoelectric point. Silanol and silane-triol functional groups would be classed as anionic surfactant groups along with carboxylates, sulfonates, etc., and would be most active toward positive surfaces, i.e., where pH is below the isoelectric point of the mineral surfaces. In an alkaline environment with pH above the isoelectric point, an alkyl silanol surfactant would be much less effective. Plueddemann (10) pointed out that a cationic silane such as Z-6020 could actually bond "upside down" to the surface through its amine group - suspending use of the silanol group. In this connection, note the high confidence level for the third-order interaction A\*C\*E in Table 16a and the 3 variable model in Table 16e.

Another possible cause of the apparent reversal of the coupler's effects on resilience in Golden Bear asphalt is the presence of a large concentration of basic nitrogen compounds in this asphalt. These compounds may tend to combine with some of the silanols and hold them back from the action at the mineral surface. This effect would perhaps be temporary. Sufficient curing time, particularly during mixing would enable equilibrium to be attained where the coupler should be found in high concentration at the interfaces. This possibility does not explain the trend in resilience of pretreated aggregates with Golden Bear.

It will be seen that the filler of higher bulk volume, Salt River, imparts a higher modulus of resilience to specimens than does Agua Fria. Also, the higher concentration of filler of each type imparts a higher value. This may

indicate that the bulk volume of a filler is a relevant property and that phase volume ratios should be considered useful in composite binder manufacturing.